

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 19-01-2012		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Jul-2006 - 31-Aug-2011	
4. TITLE AND SUBTITLE Nanoscale electronics from a molecular perspective-final annual report			5a. CONTRACT NUMBER W911NF-06-1-0266		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 662262		
6. AUTHORS Thomas P. Pearl			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES North Carolina State University Office of Contract and Grants Leazar Hall Lower Level- MC Raleigh, NC 27695 -7214			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 48407-EL.11		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT Molecular organization at surfaces impacts a broad range of fundamental and applied engineering problems in the realm of nanoscale electronics and sensing. We are capable of supplying molecular level details for nanostructured media on how chemical and physical driving forces can be controlled for the purpose of generating functional structures. Our scientific approach additionally affords us a broad range of collaborative opportunities and positions us to work closely with synthetic chemists as well as device scientists and engineers.					
15. SUBJECT TERMS molecules, surfaces, sensing, imaging					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Thomas Pearl
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 919-513-7360

Report Title

Nanoscale electronics from a molecular perspective-final annual report

ABSTRACT

Molecular organization at surfaces impacts a broad range of fundamental and applied engineering problems in the realm of nanoscale electronics and sensing. We are capable of supplying molecular level details for nanostructured media on how chemical and physical driving forces can be controlled for the purpose of generating functional structures. Our scientific approach additionally affords us a broad range of collaborative opportunities and positions us to work closely with synthetic chemists as well as device scientists and engineers.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
2012/01/05 21: 10	Pengshun Luo, Norman L. Bemelmans, Thomas P. Pearl. Unveiling Molecular Adsorption Geometry in Cyclohexanethiolate Self-Assembled Monolayers with Local Barrier Height Imaging, Journal of Physical Chemistry C, (07 2011): 0. doi:
2010/08/31 01: 9	Thomas P. Pearl. Modification of Ag ₁₁₁ ... surface electronic structure via weak molecular adsorption of adenine measured with low temperature scanning tunneling microscopy and spectroscopy, Journal of Chemical Physics, (2010): . doi:
2010/08/31 01: 8	Thomas P. Pearl. Chiral Steering of Molecular Organization in the Limit of Weak Adsorbate-Substrate Interactions, Journal of Physical Chemistry C, (2010): . doi:
2009/08/24 11: 7	Thomas P. Pearl. Reprint of paper published, Langmuir, (2009): . doi:
2009/04/06 01: 4	A.M. Lakhani, D.J. DeWitt, N.M. Sant'Agata, T.P. Pearl. Persistence of Chirality for a Weakly Bound Adsorbate: (R,R)- and (S,S)-Tartaric Acid/Ag(111), Journal of Physical Chemistry, (2007): . doi:

TOTAL: 5

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
2008/06/19 11: 6	N.M. Santagata, A.M. Lakhani, D.J. DeWitt, P. Luo, T.P. Pearl. Probing Molecular Level Organizational Structure and Electronic Decoupling of Tartaric Acid Domains Supported on Ag(111), , (): . doi:
2008/06/19 11: 5	Nancy M. Santagata, Pengshun Luo, Amit M. Lakhani, Darryl J. DeWitt, B.Scott Day, Michael L. Norton, Thomas Pearl. Organizational Structure and Electronic Decoupling of Surface Bound Chiral Domains and Biomolecules, , (): . doi:

TOTAL: 2

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):	
<u>Received</u>	<u>Paper</u>

TOTAL:
Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):	
<u>Received</u>	<u>Paper</u>

TOTAL:
Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts	
<u>Received</u>	<u>Paper</u>
2007/08/09 0: 3	N.M. Sant'Agata, A.M. Lakhani, D.J. DeWitt, P. Luo, T.P. Pearl. Probing Molecular Level Organizational Structure and Electronic Decoupling of Tartaric Acid Domains Supported on Ag(111), ()
2007/08/09 0: 2	Nancy M. Sant'Agata, Pengshun Luo, Amit M. Lakhani, Darryl J. DeWitt, B. Scott Day, Michael L. Norton, Thomas P. Pearl. Organizational Structure and Electronic Decoupling of Surface Bound Chiral Domains and Biomolecules, ()
TOTAL: 2	
Number of Manuscripts:	

Books	
<u>Received</u>	<u>Paper</u>
TOTAL:	

Patents Submitted	

Patents Awarded	

Awards	

Graduate Students	

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Shawn M. Huston	1.00	
FTE Equivalent:	1.00	
Total Number:	1	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Thomas P. Pearl	0.00	
FTE Equivalent:	0.00	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

- The number of undergraduates funded by this agreement who graduated during this period: 0.00
- The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00
- Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00
- Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

Annual (Final) Report: 1 September 2010-31 August 2011

Nanoscale electronics from a molecular perspective

ARO project: W911NF0610266

Thomas P. Pearl, Department of Physics, North Carolina State Univ., Raleigh, NC 27695-7518

Email: tppearl@ncsu.edu, Web: <http://www.physics.ncsu.edu/pearl/>

Phone: (919) 513-7360, Fax: (919) 513-0670

Cognizant ARO program manager: Dr. William Clark

Overall Project Goal:

Develop a reliable and well characterized assay for recognizing biomolecules and biomolecular species.

Research Goals:

Determine mechanisms for organization of molecular domains using high resolution scanning tunneling microscopy.

Impact of the Research:

The processes associated with how molecules form ordered structures at surfaces and interfaces is at the heart of nanoscale engineering and illumination of molecular level properties and characteristics. The impact of this work is multi-fold with dividends in determining the role that intermolecular forces play in the response of molecular thin films to applied fields for the purpose of detection or in uncovering novel approaches to harnessing molecular properties for the formation of chemical sensing and electronic junction structures.

Technology Transfers & Research Collaborations:

Our work uses model systems to inform more complex structures and the choice of molecule-surface is made to carefully highlight interactions which would be native to biomolecular or biomimetic systems: weak molecule-surface interaction and multiple hydrogen bonding interactions between molecules.

Merit of the Research: (Note that merits listed here can go outside the specific goals of the program)

Molecular organization at surfaces impacts a broad range of fundamental and applied engineering problems in the realm of nanoscale electronics and sensing. We are capable of supplying molecular level details for nanostructured media on how chemical and physical driving forces can be controlled for the purpose of generating functional structures. Our scientific approach additionally affords us a broad range of collaborative opportunities and positions us to work closely with synthetic chemists as well as device scientists and engineers.

Summary of Achievements: Tasks completed over the past year include,

- A manuscript has been accepted for publication in the Journal of Physical Chemistry-C regarding the adsorption, ordering, and local work function measurements for cyclohexanethiol on Au(111): *Unveiling Molecular Adsorption Geometry in Cyclohexanethiolate Self-Assembled Monolayers with Local Barrier Height Imaging*, Pengshun Luo, N. L. Bemelmans, T. P. Pearl, Journal of Physical Chemistry-C, in press (2011). A copy of the preprint is included as part of the report.
- Work continued on optimizing our frequency modulated atomic force microscopy system that allows for a broader array of experiments associated with biomolecular adsorption at surfaces, including enhanced collaboration with other members of the DTRA team. Significant progress was made on the implementation of a new, high gain, low noise preamplifier. Proof of performance experiments were demonstrated in both imaging modes, with a test system of bare Ag(111) and pentacene covered Ag(111).
- Preparation of 2 manuscripts are still in progress:
 - *Organizational structure of adenine monolayers grown on Ag(111) measured with low temperature scanning tunneling microscopy*, Katie M. Andrews, Bryce F. Davis, and Thomas P. Pearl, in preparation for submission to Surface Science.
 - *Influence of organic overlayer stereochemistry on interfacial electronic structure*, N. M. Santagata, A. M. Lakhani, B. F. Davis, P. Luo, A. Calzolari, Marco Buongiorno Nardelli, and T. P. Pearl, in preparation for submission to Physical Review Letters
 - The delay in completion of these papers was due to less time available for the principal researchers (former graduate students and post-doc) involved due to having relocated to other institutions as well as incorporating computational data that is still being finished to complement the experimental work.
- Experiments on the adsorption of a halogenated anthrocene molecule on Ag(111), 9,10 dibromoanthracene were performed over the past year revealing a rich and complex behavior for this weakly adsorbed species. We were interested in the uncovering the organizational properties of the weakly surface bound molecule, particularly in the limit where the halogens compete with or amplify hydrogen bonding stability in the film. This molecule is being treated as a substituted pentacene, as an electron donor, that has the potential to exhibit selective binding for a subsequently exposed species.

Summary Achievement Metrics and Statistics for “Nanoscale electronics from a molecular perspective”

1. Papers submitted or Published in Non-Peer-Review Journals	0
2. Papers submitted or published in Peer-Reviewed Journals	1
3. Book or Book Chapters Authored	0
4. Presentations at Conference or other Relevant Technical Meetings (including colloquia)	0
5. Honors and Awards	0
6. Patents	0
7. Researchers Supported	1

(please denote type (undergraduate, graduate student, post doc, etc., and enter % supported- (approximate percentages)):

Shawn M. Huston (graduate student): 100%

Current position: post-doctoral research associate, Appalachian State University, Boone, NC

Expected graduation date: May 2012

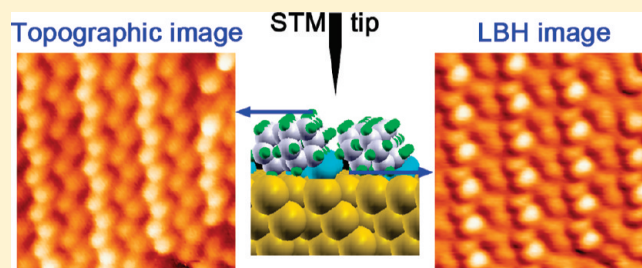
Unveiling Molecular Adsorption Geometry in Cyclohexanethiolate Self-Assembled Monolayers with Local Barrier Height Imaging

Pengshun Luo,^{*,†,‡} Norman L. Bemelmans,[§] and Thomas P. Pearl^{*,‡}

[†]School of Physics, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

[‡]Department of Physics, and [§]Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-7518, United States

ABSTRACT: The Au–S interface of thiol-based, self-assembled monolayers grown on Au(111) surfaces is far less understood than it should be. Local barrier height imaging, which has recently resolved work function variations in the buried interface of alkanethiolate monolayers, is now used to study self-assembled monolayers on Au(111) formed by cyclohexanethiol, a molecule with a flexible aliphatic ring structure. Multiple ordered phases are observed, consistent with its conformational flexibility which makes multiple interadsorbate interactions possible. In one particular phase, the appearance of two readily distinguishable features in local barrier height images implies at least two types of adsorption sites. Correlation of simultaneously acquired topographic and local barrier height data allows for a preliminary structural model that accounts for adsorption geometry.



INTRODUCTION

The growth of alkanethiolate self-assembled monolayers (SAMs) on Au(111) surfaces is one of the most intensively studied self-assembly systems in the last two decades.^{1–6} This is partially due to the easy and robust fabrication of those SAMs as well as their broad potential applications in molecular electronics, biosensors, nanofabrication, and surface protection.^{3,4,7,8} Several ordered structures have been observed as a function of surface coverage, temperature, and length of the hydrocarbon chain.^{2,9,10} For the saturation coverage of most alkanethiolate SAMs, the well-known ($\sqrt{3} \times \sqrt{3}$)R30° structure and its rectangular c(4 × 2) superlattice have been routinely observed by scanning tunneling microscopy (STM) topographic imaging^{11–14} and low energy electron diffraction (LEED).^{15,16} Unlike the surface periodic structures, which can be well characterized by STM and LEED, the underlying interface, where the sulfur headgroup is bonded to the Au surface, is far from being well understood.^{17–20} It was assumed for a long time that the sulfur headgroup would most likely adsorb on the high-symmetry 3-fold hollow-site for the ($\sqrt{3} \times \sqrt{3}$)R30° phase, while the c(4 × 2) structure was assumed to be due to adsorption on different sites.^{21–25} However, photon-electron diffraction²⁶ and near-incidence X-ray standing wave (NIXSW)²⁷ measurements indicate that the sulfur atoms most likely occupy the atop sites. Recently, more experiments using NIXSW²⁸ and grazing incidence X-ray diffraction (GIXRD)^{29,30} as well as STM imaging of individual short alkanethiolate molecules^{31–35} suggest the important role of Au adatoms, Au vacancies, and the reconstruction of the outmost layer of Au(111) in the alkanethiol adsorption. While NIXSW and GIXRD are spatially

averaged techniques, a recent local barrier height (LBH) measurement was used to image the underlying sulfur head groups with molecular resolution by STM.³⁶ In this case simultaneous imaging was performed of both the end group with topographic imaging and the sulfur headgroup with LBH imaging.

In this study, we have employed LBH imaging to investigate SAMs formed from the adsorption of a conformationally flexible molecule, cyclohexanethiol (CHT), on Au(111). The CHT molecule has a carbon ring of six carbon atoms linked by single C–C bonds, and the thiol group is attached to one of the carbon atoms. Due to the flexible aliphatic ring, the molecule has several structural conformers.³⁷ When they adsorb on the Au (111) surface, different ordered structures have been observed with ambient STM.^{38,39} Two main conformers, equatorial-chair and axial-chair, have been proposed to compose the ordered structures. The CHT SAMs have also been successfully used to grow benzenethiol monolayers by displacement of CHT molecules with benzenethiol molecules.⁴⁰ In this study, we have imaged CHT SAMs with a low temperature STM in ultrahigh vacuum. By quantitatively comparing topographic and LBH image features, we are able to unveil the underlying sulfur headgroup adsorption as well as the molecular azimuth tilt directions.

EXPERIMENTAL METHODS

CHT SAMs were grown from solution deposition on to Au/Mica substrates, a 150 nm thick Au layer thermally evaporated on to a cleaved Mica sheet (Agilent Technologies). Prior to SAM

Received: June 16, 2011

Revised: July 19, 2011

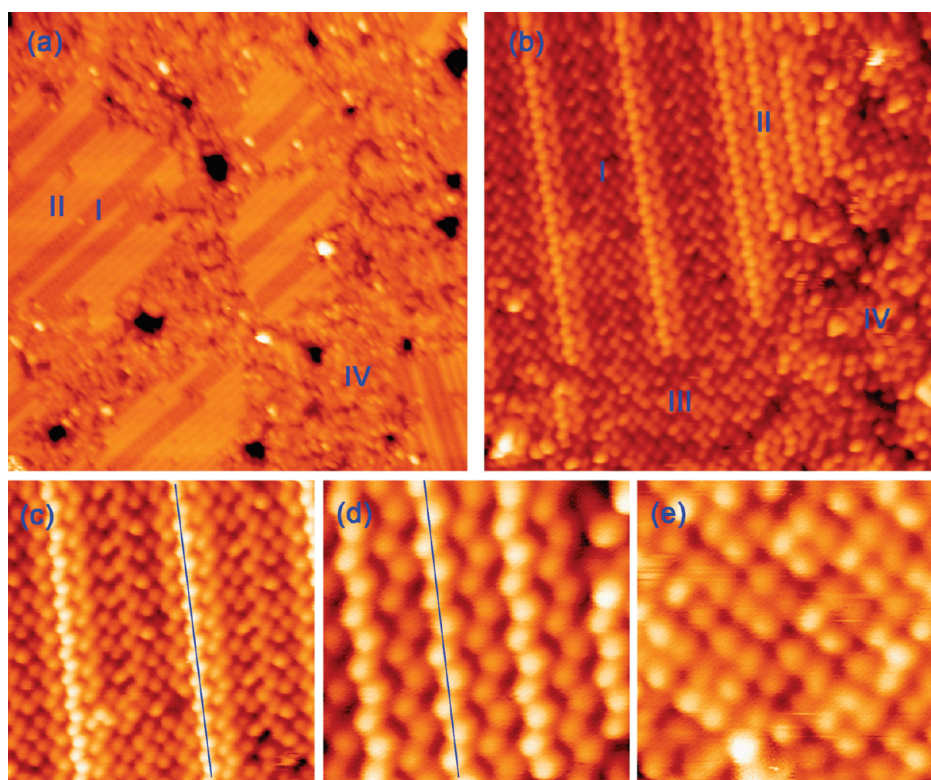


Figure 1. STM topographic images of CHT SAM on Au (111). (a) A large scale image ($75.6 \times 75.6 \text{ nm}^2$) shows vacancy islands (black holes), ordered structures (I, II, and III), and disordered molecular regions (IV). (b) $22.7 \times 22.7 \text{ nm}^2$ region with three ordered phases I, II, and III and disordered molecular layer (IV) presented. (c–e): High resolution images of phase I (c), II (d), and III (e) with image sizes: 11.3×11.3 (c) and $5.7 \times 5.7 \text{ nm}^2$ (d and e). Image acquisition conditions: $V_{\text{sample}} = 1.5 \text{ V}$, $I_t = 10$ (a) and 8 pA (b–e).

growth, the Au(111) surface was prepared with hydrogen flame-annealing of the Au layer. The substrate was then immersed in a 1 mM CHT (Sigma Aldrich, purity 97%) solution in 200 proof ethanol immediately after annealing. After 26.5 h deposition in solution, the substrate was then gently rinsed with ethanol and then dried with dry nitrogen gas. The substrate with CHT SAMs was then transferred to a custom-made low temperature scanning tunneling microscope⁴¹ housed in an ultrahigh vacuum system with a base pressure below 10^{-10} Torr. All of the measurements reported in this paper have been done at 83 K. Image processing was partially performed with WSxM, a free application developed by Nanotec Electronica S.L.⁴²

LBH images were simultaneously recorded with topographic images. During imaging, a small AC modulation voltage (1 kHz, $V_{\text{rms}} = 4\text{--}10 \text{ mV}$) was applied to the z motion (orthogonal to the surface) of the tip, which results in a (0.024–0.060 nm) amplitude oscillation of the tip–sample distance. The resultant modulated tunneling current signal is fed into a lock-in-amplifier that is then used to measure the first harmonic of the current with respect to distance (z) by phase sensitive detection. According to the electronic tunneling theory, dI/dz is approximately given by

$$\frac{dI}{dz} \approx -\frac{2\sqrt{2m}}{\hbar} \sqrt{\phi_0} \times I, \quad \phi_0 = \frac{\phi_t + \phi_s}{2} \quad (1)$$

where ϕ_t is the work function of the tip, ϕ_s is the local work function of the sample, and ϕ_0 is the effective LBH of the tunneling junction. In constant current mode, dI/dz is directly proportional to the square root of effective LBH, so the LBH

image in this paper is referred to as the dI/dz image in constant current mode.

RESULTS AND DISCUSSION

Multiple phases are observed for the CHT SAM as shown in a typical large scale image of the SAM (see Figure 1a). In contrast to long chain alkanethiolate SAMs, a large portion of the CHT monolayer is disordered (region IV). This is most likely due to its flexible aliphatic ring structure and relatively short molecular length. Inside the disordered area, we observe vacancy islands resulting from sulfur driven abstraction of Au surface atoms, similar to those that occur in other thiol anchored SAMs on Au. In addition to the disordered regions, three ordered structures are also observed. Phases I and II are the two ordered structures that occur most readily. Both phases exhibit zigzag molecular rows. Most molecules of phase I appear darker (lower height) than those of phase II in topographic images (Figure 1a–d). In phase II, as shown in Figure 1d, the molecules are packed in alternatingly bright and dark zigzag molecular rows. The dark area in phase I is separated by the bright zigzag molecular rows which have the same contrast in topography and ordering as the bright rows in phase II. Apart from these two phases, in a few surface areas, we are able to observe the third phase as shown in Figure 1, panels b and e. In the third phase, the molecules form a distorted monoclinic lattice and individual molecules in this phase occasionally exhibit different topographic contrast.

The topographic image is a measure of the convolution of surface crystal structure and local density of electronic states.

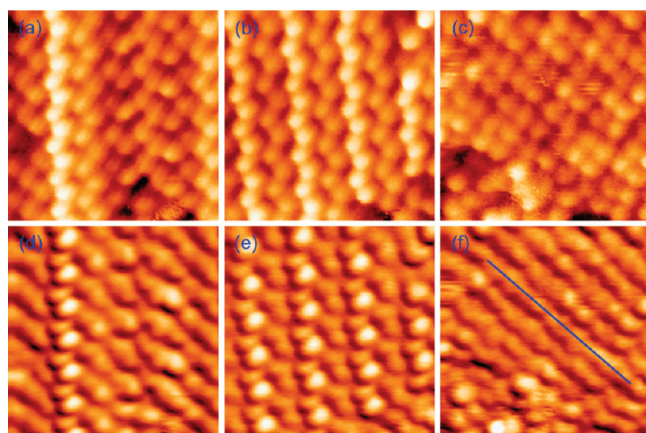


Figure 2. STM topographic images (a–c) and simultaneously recorded LBH images (d–f) for phases I, II, and III. Image areas: $5.7 \times 5.7 \text{ nm}^2$. Image acquisition conditions: $V_{\text{sample}} = 1.5 \text{ V}$, $I_t = 8 \text{ pA}$. Modulation voltages used for the dI/dz measurements: $V_{\text{rms}} = 8 \text{ mV}$ (a and d), $V_{\text{rms}} = 4 \text{ mV}$ (b, c, e, and f), $f_{\text{mod}} = 1 \text{ kHz}$.

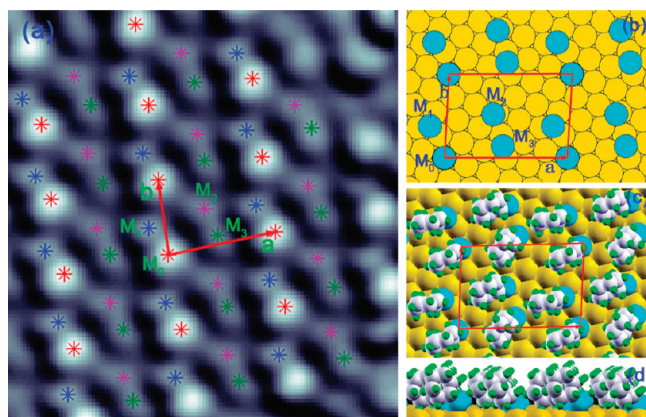


Figure 3. (a) LBH image of phase II. The “*” indicate the local maxima. M_1 , M_2 , and M_3 indicate the three bright features other than the brightest one (M_0) in a unit cell. (b) The adsorption sites of the CHT molecules on the Au (111) are presented with information derived from the experimental data. (c) Top view of the preliminary structural model of phase II showing the adsorption sites and adsorbate azimuth orientation. (d) Side view of the preliminary structural model of phase II showing the alternating higher and lower molecular rows.

In most cases, when the spatial variation of surface electronic structure, i.e., local density of states, is uniform, the topographic image represents the surface morphology. In other words, we usually image the top part, or exposed surface, of the molecular monolayer by topographic imaging. On the other hand, LBH imaging is sensitive to variations in the LBH of the tunneling junction as a function of position. When the sulfur headgroup adsorbs on the Au(111) surface, the formation of the sulfur–Au covalent bond modifies the surface local work function and the local tunneling barrier height distinctly.⁴³ This gives us an opportunity to resolve the sulfur atom position at the S–Au interface relative to the position of the exposed molecular positions in a fashion similar to what was reported in the literature.³⁶

Both STM topographic images and LBH images were recorded for the three ordered phases. Figure 2 shows that the LBH

Table 1. Lists of the local maxima position (x_a and x_b) in the LBH image, the distance (d) between the local maxima in topographic image and LBH image, and molecular tilt azimuth angle (α) referred to the unit cell vector a^a

	x_a	x_b	d (nm)	α (°)
M_0	0	0	0.39	209
M_1	−0.13	0.38	0.29	192
M_2	0.38	0.52	0.31	188
M_3	0.47	0.14	0.25	218

^a (x_a , x_b) is in relation to the unit cell vectors.

images appear quite different from the topographic images. A common characteristic of both phases I and II is that some features are much brighter, i.e., higher LBH intensity, than others. The different brightness is most likely due to inequivalent adsorption sites of the sulfur headgroup since the charge transfer varies as a function of sulfur headgroup adsorption site.^{36,43} Furthermore, the features in the LBH image are elliptical in shape rather than circular as seen in the topographic images for the same feature. It is also interesting to note that the molecular row with the brightest features in phase I has the same appearance as that of phase II in the LBH images, which demonstrates again that the same ordering of the bright molecular rows exists between phases I and II. In phase III, the features form separated rows along the line direction as marked in Figure 2(f). Due to the well observed periodicity of phase II, we will focus our following discussion on this phase.

From analysis of both the topographic images and LBH images after drift correction, the 2D lattice constant of phase II is determined to be $a = 1.47 \pm 0.02 \text{ nm}$ and $b = 1.03 \pm 0.02 \text{ nm}$. The angle between the vector a and b is $\gamma = 87 \pm 1^\circ$ (see Figure 3). The drift rate is assumed to be constant and calculated between two successively recorded images. The unit cell for phase II corresponds to a $2\sqrt{7} \times \sqrt{13}19.1^\circ$ structure with respect to the unreconstructed Au(111) surface (see Figure 3c).

The local maxima in the LBH image are searched by the Matlab program used in ref 36. We name the brightest features M_0 , and the other three features in the unit cell M_1 , M_2 , M_3 as indicated in Figure 3a. The coordinates (x_a , x_b in Table 1) of the local maxima of M_0 , M_1 , M_2 , and M_3 are then calculated in the unit cell coordinate system. Assuming the M_0 locations are the sulfur headgroup adsorbed on the atop site of Au(111) surface, we are able to reproduce the features observed in the LBH image on an unreconstructed Au(111) surface. As shown in Figure 3b, all of the features (M_1 , M_2 , M_3) other than M_0 are located near the bridge sites. This is consistent with the brightness differences between M_0 and M_1 , M_2 , M_3 . We also considered other possibilities such as M_0 adsorbing on the hcp, fcc hollow sites or the bridges sites, and then tried to reproduce M_1 , M_2 , M_3 on the Au (111) surface lattice. None of these possibilities is consistent with the LBH image as well as M_0 adsorbed on the atop site.

With the adsorption site determined, the molecular tilt direction (azimuth angle) can be calculated by quantitatively comparing the topographic and the LBH images. With the same Matlab program, the local maxima in the topographic image are determined and marked as “*” in both the topographic image and the LBH image in Figure 4. Since the length of the long axis of the molecule is much shorter than the alkanethiol molecules used in ref 36, we need only to consider the possibility that the nearest

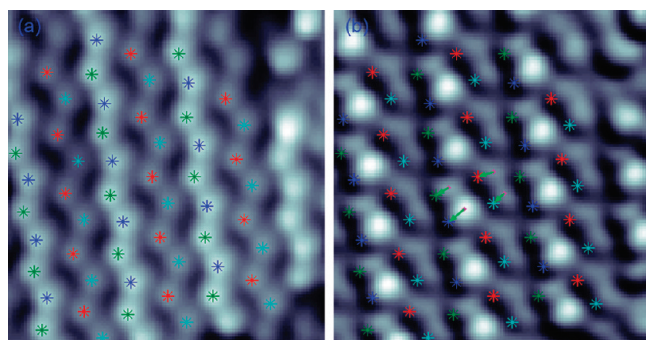


Figure 4. STM topographic image (a) and LBH image (b) recorded simultaneously for phase II. The local maxima in the topographic image are marked as “*” and are also marked in the LBH image. The arrows in (b) point from the local maxima of the LBH image to the local maxima of the topographic image.

topographic maxima around the LBH maxima belong to the same molecule. With this in mind, the molecular tilt direction is determined as indicated by the arrows in Figure 4 which point from the local LBH maxima to the nearest topographic maxima, and the azimuth angle (α) refers to the vector \mathbf{a} as listed in Table 1. The distance between the topographic maxima and the LBH maxima are calculated and listed in Table 1 as well. Further examination of the shape of the features in the LBH image finds that the long axis of the elliptical shapes is along the tilt direction for M_0 , M_1 , and M_2 , but not for M_3 . It should be noted that according to the molecular azimuth angle measured with respect to the Au(111) $\langle 110 \rangle$ direction in ref 36, the long axis of the elliptical features in the LBH image is approximately along the molecular tilt direction for the alkanethiolate SAMs too (Figure 3b in ref 36). The reason for this needs further theoretical calculation, but we may propose the following reasonable explanation. As the charge transfer most likely occurs along the C–S–Au bonds, we expect that the LBH modification occurs not only on the sulfur atom but also along the C–S–Au bonds. For M_0 , M_1 , M_2 , the C–S–Au bonds tilt along the molecular tilt direction while for M_3 the C–S–Au bonds might be nearly standing up. This might explain why M_3 appears smaller in LBH image compared to other molecules in the unit cell. Due to this effect, we should bear in our mind that the real sulfur anchoring sites might be offset from the local maxima of the LBH features.

Based on the above analysis, a preliminary structural model of phase II can be proposed as shown in Figure 3, panels c (top view) and d (side view). In this model, we reproduce the sulfur adsorption sites on an unreconstructed Au(111) surface according to the experimental observations, which means that one molecule adsorbs on the atop site and the other three molecules adsorb on the near bridge sites. The molecular tilt direction (azimuth angle) is also derived from the experimental data, while the polar angle of the molecular tilt direction needs to be further optimized by a structural relaxation calculation. The molecular aliphatic ring plane cannot be determined from the experimental data either, but is assumed to be vertical with respect to the Au(111) surface for the higher molecular rows as a start for the structural relaxation. In order to reproduce the alternative higher and lower molecular rows appearing in the topographic images, the aliphatic ring plane at the lower row should be rotated around the long axis comparing to the higher rows (see Figure 3, panels c and d).

CONCLUSIONS

In summary, we have investigated CHT SAMs grown from solution on Au(111) with a low temperature STM in ultrahigh vacuum. Multiple structural phases of the monolayer have been observed for this conformationally flexible molecule. LBH imaging has been applied to reveal the underlying adsorption arrangement. Based on the simultaneous topographic and the LBH imaging, molecular adsorption sites as well as the azimuth angles have been determined. Although we are not able to give a final structural model based on the experimental data, we propose a preliminary model which would be a good start for further theoretical structure optimization. Our experimental result demonstrates again the capability of the LBH imaging, particularly in unveiling the adsorption sites in the complex self-assembled monolayers such as CHT SAMs.

AUTHOR INFORMATION

Corresponding Author

*E-mail: plu02009@mail.hust.edu.cn; tppearl@ncsu.edu.

ACKNOWLEDGMENT

Support from the Army Research Office and the Defense Threat Reduction Agency, Grant No. W911NF-06-1-0266, as well as the National Science Foundation, DMR-0403871, is gratefully acknowledged.

REFERENCES

- (1) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481–4483.
- (2) Poirier, G. E. *Chem. Rev.* **1997**, *97*, 1117–1127.
- (3) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103–1169.
- (4) Smith, R. K.; Lewis, P. A.; Weiss, P. S. *Prog. Surf. Sci.* **2004**, *75*, 1–68.
- (5) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533–1554.
- (6) Schreiber, F. *Prog. Surf. Sci.* **2000**, *65*, 151–256.
- (7) Gates, B. D.; Xu, Q.; Stewart, M.; Ryan, D.; Willson, C. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1171–1196.
- (8) Azzaroni, O.; Cipollone, M.; Vela, M. E.; Salvarezza, R. C. *Langmuir* **2001**, *17*, 1483–1487.
- (9) Camillone, N.; Leung, T. Y. B.; Schwartz, P.; Eisenberger, P.; Scoles, G. *Langmuir* **1996**, *12*, 2737–2746.
- (10) Rosenbaum, A. W.; Freedman, M. A.; Darling, S. B.; Popova, I.; Sibener, S. J. *J. Chem. Phys.* **2004**, *120*, 3880–3886.
- (11) Widrig, C. A.; Alves, C. A.; Porter, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 2805–2810.
- (12) Poirier, G. E.; Tarlov, M. J. *Langmuir* **1994**, *10*, 2853–2856.
- (13) Delamarche, E.; Michel, B.; Gerber, C.; Anselmetti, D.; Guentherodt, H. J.; Wolf, H.; Ringsdorf, H. *Langmuir* **1994**, *10*, 2869–2871.
- (14) Poirier, G. E.; Pylant, E. D. *Science* **1996**, *272*, 1145–1148.
- (15) Strong, L.; Whitesides, G. M. *Langmuir* **1988**, *4*, 546–558.
- (16) Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Chem. Phys.* **1993**, *98*, 678–688.
- (17) Maksymovych, P.; Voznyy, O.; Dougherty, D. B.; Sorescu, D. C.; Yates, J. T. *Prog. Surf. Sci.* **2010**, *85*, 206–240.
- (18) Woodruff, D. P. *Phys. Chem. Chem. Phys.* **2008**, *10*, 7211–7221.
- (19) Vericat, C.; Vela, M. E.; Benitez, G.; Carro, P.; Salvarezza, R. C. *Chem. Soc. Rev.* **2010**, *39*, 1805–1834.
- (20) Fenter, P.; Eberhardt, A.; Eisenberger, P. *Science* **1994**, *266*, 1216–1218.
- (21) Torrelles, X.; Vericat, C.; Vela, M. E.; Fonticelli, M. H.; Daza Millone, M. A.; Felici, R.; Lee, T.-L.; Zegenhagen, J.; Muñoz, G.; Martín-Gago, J. A.; Salvarezza, R. C. *J. Phys. Chem. B* **2006**, *110*, 5586–5594.

- (22) Torrelles, X.; Barrena, E.; Munuera, C.; Rius, J.; Ferrer, S.; Ocal, C. *Langmuir* **2004**, *20*, 9396–9402.
- (23) Fischer, D.; Curioni, A.; Andreoni, W. *Langmuir* **2003**, *19*, 3567–3571.
- (24) Yourdshahyan, Y.; Rappe, A. M. *J. Chem. Phys.* **2002**, *117*, 825–833.
- (25) Vargas, M. C.; Giannozzi, P.; Selloni, A.; Scoles, G. *J. Phys. Chem. B* **2001**, *105*, 9509–9513.
- (26) Kondoh, H.; Iwasaki, M.; Shimada, T.; Amemiya, K.; Yokoyama, T.; Ohta, T.; Shimomura, M.; Kono, S. *Phys. Rev. Lett.* **2003**, *90*, 066102.
- (27) Roper, M. G.; Skegg, M. P.; Fisher, C. J.; Lee, J. J.; Dhanak, V. R.; Woodruff, D. P.; Jones, R. G. *Chem. Phys. Lett.* **2004**, *389*, 87–91.
- (28) Yu, M.; Bovet, N.; Satterley, C. J.; Bengi, oacute, S.; Lovelock, K. R. J.; Milligan, P. K.; Jones, R. G.; Woodruff, D. P.; Dhanak, V. *Phys. Rev. Lett.* **2006**, *97*, 166102.
- (29) Mazzarello, R.; Cossaro, A.; Verdini, A.; Rousseau, R.; Casalis, L.; Danisman, M. F.; Floreano, L.; Scandolo, S.; Morgante, A.; Scoles, G. *Phys. Rev. Lett.* **2007**, *98*, 016102.
- (30) Cossaro, A.; Mazzarello, R.; Rousseau, R.; Casalis, L.; Verdini, A.; Kohlmeier, A.; Floreano, L.; Scandolo, S.; Morgante, A.; Klein, M. L.; Scoles, G. *Science* **2008**, *321*, 943–946.
- (31) Maksymovych, P.; Sorescu, D. C.; Yates, J. T. *Phys. Rev. Lett.* **2006**, *97*, 146103.
- (32) Kautz, N. A.; Kandel, S. A. *J. Am. Chem. Soc.* **2008**, *130*, 6908–6909.
- (33) Maksymovych, P.; Yates, J. T. *J. Am. Chem. Soc.* **2008**, *130*, 7518–7519.
- (34) Voznyy, O.; Dubowski, J. J.; Yates, J. T.; Maksymovych, P. *J. Am. Chem. Soc.* **2009**, *131*, 12989–12993.
- (35) Li, F. S.; Tang, L.; Zhou, W. C.; Guo, Q. M. *J. Am. Chem. Soc.* **2010**, *132*, 13059–13063.
- (36) Han, P.; Kurland, A. R.; Giordano, A. N.; Nanayakkara, S. U.; Blake, M. M.; Pochas, C. M.; Weiss, P. S. *ACS Nano* **2009**, *3*, 3115–3121.
- (37) Scott, D. W.; Crowder, G. A. *J. Chem. Phys.* **1967**, *46*, 1054–1062.
- (38) Noh, J.; Hara, M. *Langmuir* **2002**, *18*, 9111–9115.
- (39) Kwon, S.; Jeong, Y.; Lee, Y.; Noh, J. *Chem. Lett.* **2007**, *36*, 390–391.
- (40) Kang, H.; Lee, H.; Kang, Y.; Hara, M.; Noh, J. *Chem. Commun.* **2008**, 5197–5199.
- (41) Lakhani, A. M.; Kelly, S. J.; Pearl, T. P. *Rev. Sci. Instrum.* **2006**, *77*, 043709.
- (42) Horcas, I.; Fernandez, R.; Gomez-Rodriguez, J. M.; Colchero, J.; Gomez-Herrero, J.; Baro, A. M. *Rev. Sci. Instrum.* **2007**, *78*, 013705.
- (43) Marchon, B.; Bernhardt, P.; Bussell, M. E.; Somorjai, G. A.; Salmeron, M.; Siekhaus, W. *Phys. Rev. Lett.* **1988**, *60*, 1166.